

# Transport and Fate of Methyl Iodide and Its Pest Control in Soils

LIFANG LUO,<sup>\*,†,‡</sup> DANIEL ASHWORTH,<sup>†</sup>  
ROBERT S. DUNGAN,<sup>§</sup> RICHENG XUAN,<sup>†,‡</sup>  
AND SCOTT R. YATES

U.S. Salinity Laboratory, 450 West Big Springs Road,  
Riverside, California 92507, Department of Environmental  
Sciences, University of California, Riverside, California 92507,  
and USDA-ARS, Northwest Irrigation and Soils Research  
Laboratory, 3793 N 3600 E, Kimberly, Idaho 83341

Received January 26, 2010. Revised manuscript received  
June 15, 2010. Accepted June 28, 2010.

For fumigants, information on transport and fate as well as pest control is needed to develop management practices with the fewest negative environmental effects while offering sufficient pest control efficacy. For this purpose, a 2-D soil chamber with a surface-mounted flux chamber was designed to determine volatilization, real-time soil gas-phase concentration, degradation, and organism survivability after methyl iodide (MeI) fumigation. Three types of pests were used to give a broad spectrum of pest control information. An infected sandy loam soil with a volumetric water content of 10.6% was packed carefully into the 2-D chamber to a bulk density of  $1.34 \text{ g cm}^{-3}$ . After MeI fumigation at a rate of  $56.4 \text{ kg ha}^{-1}$  for 24 h, about 28.9% of MeI was emitted into air, 6.8% remained in the soil, and 43.6% degraded in the soil (based on the residual iodide concentration). The uncertainty in the measured MeI degradation using iodide concentration was thought to mainly contribute to the unrecovered MeI (about 20%). The citrus nematodes [*Tylenchulus semipenetrans*] were effectively eliminated even at low concentration–time (CT) values ( $<30 \mu\text{g h mL}^{-1}$ ), but all *Fusarium oxysporum* survived. The response of barnyardgrass seeds [*Echinochloa crus-galli*] spatially varied with the CT values in the chamber. To fully control barnyardgrass seeds, CT of greater than  $300 \mu\text{g h mL}^{-1}$  was required. Using this experimental approach, different fumigant emission reduction strategies can be tested, and mathematical models can be verified to determine which strategies produce the least emission to the atmosphere while maintaining sufficient pest control efficacy.

## Introduction

Fumigants are widely used to control soil-borne diseases and optimize crop yields. However, the adverse human and environmental health risks of their agricultural use have caused increasing concern. Methyl bromide (MeBr) use was phased out before 2005 because it is an ozone-depleting chemical, and, currently, only three fully registered fumigants remain. The use of fumigants is strictly controlled under federal and state regulations. An ideal chemical alternative

to MeBr would have fewer or no human and environmental health risks while offering sufficient pest control efficacy.

There has been extensive research on fumigant volatilization (1–4) because a significant fraction (about 20–80%) of applied fumigants can be emitted into the atmosphere after fumigation (2–4) and increase the health risk to agricultural workers and people nearby. Many pesticides are considered to be carcinogenic (5). To minimize air pollution from soil fumigation, various approaches have been developed to reduce fumigant emissions to the atmosphere, such as less permeable films, surface irrigation, organic matter addition, and fertilizer addition (e.g. refs 3, 4, and 6–8). However, little has been known about the effects of these emission reduction strategies on pest control efficacy, which require long-term testing.

Dose–response curves of pests to pesticides have been examined in soil to evaluate their efficacy (9, 10). However, even with the same application rate and type of soil, pesticide concentration in soil varies with different application methods, procedures, and conditions. Therefore, the dose–response curve itself cannot be used to accurately evaluate various application methods for disinfecting soils and reducing fumigant emission; quantitative information on both fumigant movement in the soil and its efficacy of pest control is required.

Few studies have provided quantitative information on both fumigant movement, particularly the spatial and temporal distribution, and its efficacy of pest control. Wang and Yates (11) measured spatial and temporal distribution of 1,3-dichloropropene (1,3-D) concentration in the soil after fumigation and found a 1,3-D threshold CT value of  $12 \mu\text{g h mL}^{-1}$  to reach a 100% efficacy toward citrus nematodes. Large-scale field experiments to determine fumigant movement and pest control are very time-consuming and costly. The comparisons of emission rates from large-scale field experiments and laboratory soil column experiments have shown that some field-scale processes can be reasonably duplicated by the well-controlled laboratory experiments (12). An experimental system allowing measurement of real-time volatilization and concentration was designed to examine the dynamics of volatile pesticide transport and fate in soil (13).

Methyl iodine, a potential alternative to MeBr, provides even more efficacy than MeBr in controlling soil pathogens (14, 15) but does not deplete ozone in the stratosphere (16). The objective of this study was to describe a protocol to determine MeI volatilization, degradation, spatiotemporal variation in the soil, and its pest control in an improved 2-D soil column.

## Methodology

**Soil and Pathogen Preparations.** The soil used in the study was mapped as Milham sandy loam (fine-loamy, mixed, superactive, thermic Typic Haplargids). The soil consisted of 60% sand, 30% silt, 10% clay, and 2.5% organic matter. The soil was collected to a depth of about 20 cm from a farm site near Buttonwillow, CA. After air-drying, the soils were passed through 2-mm sieve and stored at  $5^\circ\text{C}$  for use.

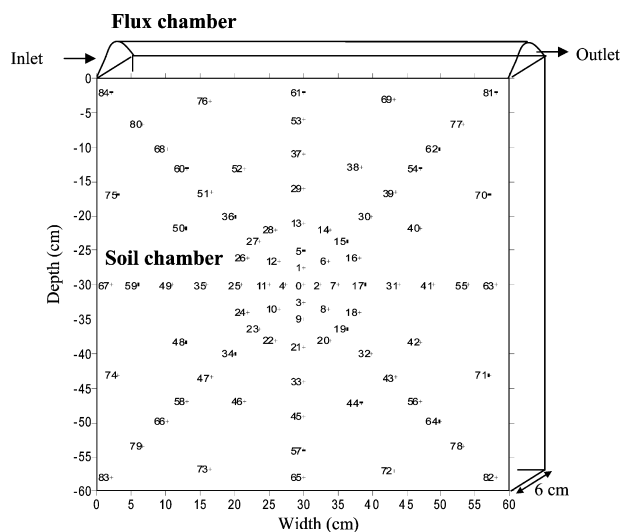
Many crops are susceptible to soil-borne pathogenic fungi and parasitic nematodes as well as competition from weeds. Two types of pathogens (citrus nematode [*T. semipenetrans*] and fungi [*F. oxysporum*]) and one type of weed seeds (barnyardgrass seed [*E. crus-galli*]) with different levels of sensitivity to MeI were used to provide a broad range of pest control information. The procedure of Ma et al. (10) was followed to incubate *F. oxysporum* onto millet seeds. Before

\* Corresponding author phone: (951)369-4847; fax: (951)342-4964; e-mail: Lifang.luo@ars.usda.gov.

<sup>†</sup> U.S. Salinity Laboratory.

<sup>‡</sup> University of California.

<sup>§</sup> USDA-ARS.



**FIGURE 1. Schematic of the 2-D experimental system consisting of a rectangular soil chamber, a surface-mounted flux chamber, and numerous sampling ports surrounding the injection port.**

the experiment, the citrus nematodes (*T. semipenetrans*) were collected from the citrus roots of an infested orchard at the University of California, Riverside Citrus Research Center, CA. Infested citrus roots were cut into small pieces, passed a 2-mm sieve, and mixed thoroughly with the soil. The citrus nematode density in the soil after mixing was examined to ensure abundant nematodes levels (>600 nematodes in 50 g soil) by extracting the nematodes using a Baermann funnel method (17). The barnyardgrass seeds (*E. crus-galli*) were purchased from Valley Seed Service, Fresno, CA. The seeds were tested and gave a germination rate of 78% at 22 °C.

**2-D Soil Chamber System.** A modified 2-D system consisting of a 2-D soil chamber and a surface-mounted flux chamber (13) was used for determining fumigant volatilization, spatial, and temporal distribution of soil gas concentration, degradation, and organism survivability (Figure 1). The soil chamber was fabricated from 0.5-cm stainless steel. The internal dimension of the soil chamber was 60 cm wide, 60 cm long, and 6 cm thick so that typical agricultural management and practice methods within the root zone could be simulated. 84 sampling ports extended radially from the central injection port so that soil gas concentration could be determined in real time. The sampling ports were made of a 2-mm brass tube fitting (San Diego Valve and Fittings Co., San Diego, CA) with the interior sealed with a 3-mm-thick by 3-mm-diameter Teflon-coated septa (Supelco, Bellefonte, PA). The surface-mounted flux chamber with a sampling section of 60 cm × 6 cm was made of galvanized sheet metal and was dome-shaped to minimize the dead space (i.e., zero or low velocity zones) when drawing and sampling air across the soil surface to measure fumigant emission.

Epoxy resin (Permalite Plastics Corp., Costa Mesa, CA) was used to prevent the leakage between the stainless steel wall and the fitting. The five stainless steel walls of the soil chamber and the base of the flux chamber were joined together using epoxy resin along the seams and bolts at the side walls. All seams were then further sealed with aluminum tape. A preliminary experiment was conducted to confirm the leak-proof nature of the system by pressurizing the sealed chamber, submerging it in water, and testing for leaking air.

**Experimental Procedures Using 2-D Soil Chamber.** Before packing, the soil (35 kg), millet seeds (80 g), barnyardgrass seeds (150 g), and nematode roots (2100 g) were mixed thoroughly to ensure that sufficient seeds and nematodes were contained in the soil samples (about 75 cm<sup>3</sup>) to be taken at the end of experiment. The final water content of the soil was 7.9% by weight. The infected soil was

packed carefully into the 2-D chamber to a bulk density of 1.34 g cm<sup>-3</sup>. During the experiment, room temperature was at about 23 °C. Infected soil was also placed in a metal container with the same bulk density but not fumigated to provide nontreated control information.

100 µL of MeI with 99% purity (Chem Service, West Chester, PA) was injected into the soil through the central port of the 2-D system. The application rate is equivalent to a rate of 56.4 kg ha<sup>-1</sup>, about one-third of the common field application rate. The low application rate was used to obtain a relatively high variation in organism response to MeI within the chamber. After injection, gas samples were taken at 0.5, 1.5, 2.5, 3.5, 4.5, 6, 8, and 24 h using gastight 100-µL syringes (Valco Instruments Co. Inc., Baton Rouge, LA). Only 49 ports were selected for sampling to obtain a satisfactory number of samples within a relatively short time. 49 syringes were inserted into the relevant sampling ports, and a 100 µL soil gas sample was withdrawn into the syringe in a sequence of ascending port number. With the same sequence, the syringes were pulled out, and the gas samples were transferred to 12-mL vials which were capped immediately. For each run, about 6 min were taken to fill all the syringes and 6 min to transfer all the gas samples into the vials.

Immediately after fumigant injection, air in the flux chamber was pulled through the outlet tube by a vacuum at a rate of 430 mL min<sup>-1</sup>. At this rate, the air in the flux chamber was replaced about every 3 min, comparable with that of Ashworth et al. (about 3 min (4)) and Ashworth et al. (about 4.5 min (18)). This flow rate ensures no significant pressure deficit with the chamber, with respect to the ambient pressure (19). At the inlet, a charcoal filter (226-09, SKC inc., Eighty Four, PA) was used to ensure that clean air entered the flux chamber. At the outlet, an array of Teflon tubing connected to charcoal filters was used to collect the MeI emission from the soil surface. A chain of two charcoal filters, connected in series, was used to reduce the potential of MeI breakthrough. A solenoid multiposition valve (Valco Instruments Company Inc., Houston, TX) was automatically controlled by a CR3000 data logger (Campbell Scientific Inc., Logan, UT) to switch between chains of tubes at an interval of 1 h during the first 8 h and then at an interval of 2 h during the following 16 h. The sampling system was tested and found to be leak-proof.

After 24 h, the experiment was terminated, and one of the side walls (60 cm × 60 cm) of the soil chamber was removed. 49 soil samples were immediately taken with a stainless steel ring with a 4-cm diameter at the 49 ports. Meanwhile, three soil samples were also taken from the metal container as nontreated controls. The soil samples were sieved, and 36 barnyardgrass seeds and 10 millet seeds were quickly picked from each soil sample within the fume hood. 50 g of soil was used for nematode analysis, and 10.5 g of soil (moisture about 5% by weight) was used to determine iodide concentration and, hence, MeI degradation.

Citrus nematodes were extracted and enumerated under a microscope. Ten *Fusarium oxysporum*-infested millet seeds were placed onto a PDA media in a Petri dish at 22 °C. The growth of fungi was monitored daily, and the number of millet seeds colonized with fungi was counted after 5 days. The germination of 36 barnyardgrass seeds placed on a moist blotter in a Petri dish was tested at 22 °C, and germinated seeds were counted after 5 days. The mortality was calculated as the ratio of the amount of dead organisms to the amount of alive organisms in the control condition. Because of the incomplete germination of barnyardgrass seeds, the mortality (%) of barnyardgrass seeds at a certain point was calculated as

$$Mortality(x, z) = \left(1 - \frac{survival(x, z)}{survival_{control}}\right) \times 100\% \quad (1)$$

where  $x, z$  are the spatial coordinates; and  $survival_{control}$  and  $survival(x, z)$  are the germination ratio of the seeds without fumigation (control) and after fumigation at one sample location, respectively.

**Degradation Experiment.** Within the soils, degradation is one of the most important factors controlling MeI transport and fate. Therefore, a separate experiment was conducted to measure MeI degradation over time using the same soil (i.e., mixed with millet seeds, barnyardgrass seeds, and citrus nematode roots) and at the same application rate of MeI and environmental condition (i.e., at 23 °C and the 7.9% water content by weight) as the 2-D system experiment. 10.8 g of moist soil was placed in 21-mL glass vials, and 193.5  $\mu\text{g}$  of MeI was added to each vial that was immediately capped with a Teflon-coated rubber septum and aluminum crimp seal. At 0, 0.5, 1.5, 2.5, 3.5, 4.5, 6, 8, 24 h (the same intervals as soil gas sampling of the 2-D soil chamber experiment), three duplicate vials were placed at  $-19$  °C to prevent any further MeI degradation. For MeI extraction, the frozen vials were decapped, and 10 g of anhydrous sodium sulfate and 10 mL of ethyl acetate were quickly added before immediate recapping. The vials were then shaken for 1 h. After settling, 1.5 mL of supernatant solution was transferred quickly to gas chromatography (GC) vial for analysis. The degradation rate constant and half-life were determined by fitting the first-order kinetic equation to the data.

**Chemical Analyses.** Soil gas samples were analyzed using a Hewlett-Packard HP6890 GC coupled with a microelectron capture detector and a G1888 Network Headspace Sampler (Agilent Technologies, Santa Clara, CA). The column was a J&W DB-VRX30  $\text{m} \times 0.25 \text{ mm} \times 1.4 \mu\text{m}$  capillary column (Agilent Technologies, Santa Clara, CA) running at a flow rate of  $1.4 \text{ mL min}^{-1}$  and with He as the carrier gas. The inlet temperature was 240 °C, and the detector temperature was 280 °C. The GC oven temperature was maintained at 45 °C for 1 min after sample injection, increasing to 80 °C at a rate of  $2.5 \text{ }^{\circ}\text{C min}^{-1}$ . Under these conditions, the retention time of MeI was 3.67 min.

The charcoal filters were extracted by transferring the charcoal into 21-mL glass vials and adding 6 mL acetone. The vials were immediately capped with a Teflon-coated rubber septum and aluminum crimp seal and shaken for 0.5 h. After settling, the supernatant solution (around 1.5 mL) was quickly transferred to a GC vial for analysis. The same GC condition as those described above was used. Separate experiments showed that the recovery ratio of MeI using this method was about 78% and was used to correct the emission rate.

For iodide concentration measurements, 10 mL of DI water was added to each vial with 10.5 g of soil. As for standards, 1 mL of potassium iodide solution with various known concentrations and 9 mL of DI water were added to each vial with 10.5 g of soil to minimize the influence of the adsorption of iodide onto soil particles during the extraction. After capping, the vials were shaken for 1 h. After settling overnight, the supernatant solution was transferred quickly to an ion chromatography (IC; Metrohm USA Inc., Riverview, FL) vial for analyses.

**Concentration–Time Index.** To quantify organism exposure to pesticides, a concentration–time index,  $CT$ , the integral of concentration over time, is defined as

$$CT(t) = \int_0^t C_T(x, y, z, t) dt \quad (2)$$

where  $C_T(x, y, z, t)$  is the total concentration ( $\mu\text{g mL}^{-1}$ ), and  $t$  is time (h). A logistic dose–response curve was used to describe the relationship between organism mortality,  $y$ , and  $CT$

$$y = C + \frac{D - C}{1 + \left(\frac{CT}{EC_{50}}\right)^{-b}} \quad (3)$$

where  $D$  and  $C$  are the upper and lower limits of the curve (for this study,  $C$  and  $D$  were 0 and 100%, respectively),  $b$  is the slope at the inflection point of the logistic curve, and  $EC_{50}$  is the effective  $CT$  required to give a 50% of mortality.

Surfer 8 (Golden Software inc., Golden, CO) was used to map the distribution of soil gas-phase concentration, iodide concentration, and mortality of organisms. The kriging method was used to interpolate the data.

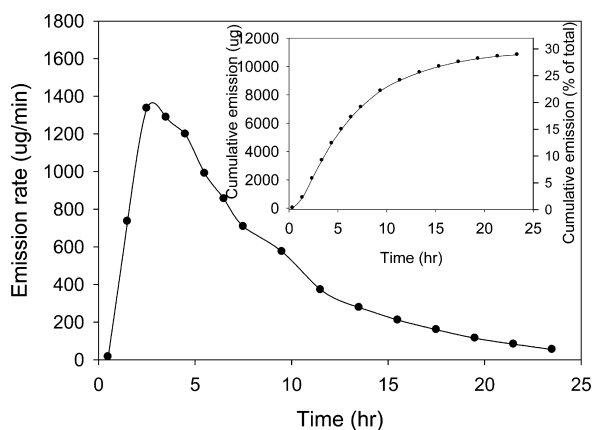
## Results and Discussion

**MeI Volatilization.** Due to the high vapor pressure (400 mmHg @ 20 °C) and Henry's constant (0.21 @ 20 °C) of MeI (20), it can readily volatilize and penetrate the soil. A half hour after injection, the measured volatilization flux of MeI from soil surface increased rapidly until around 3 h, when it reached a peak value of approximately  $1336 \mu\text{g min}^{-1}$  (Figure 2). After this time, the flux density decreased gradually. As expected, the flux curve showed an extensive tail. Gan et al. (21) reported that the peak of MeI volatilization flux was reached after about eight hours from injection into the middle depth of a soil column (62 cm in height and 12.5 cm in diameter) under nontarped conditions. The total mass of MeI volatilization recovered by charcoal filter was about 28.9% of the total injection mass. This value was lower than that reported by Gan et al. (21) who found that for a sand loam soil with 0.9% organic matter, 78% of MeI emitted into air without plastic tarp after 20 days. The low fraction of total emission was likely caused by the high degradation rate of MeI in the soil and the geometry of the 2-D chamber of this study. Compared to a 1-D system with the vertical concentration gradients, MeI within the 2-D chamber moves less vertically due to the approximately radial concentration gradients.

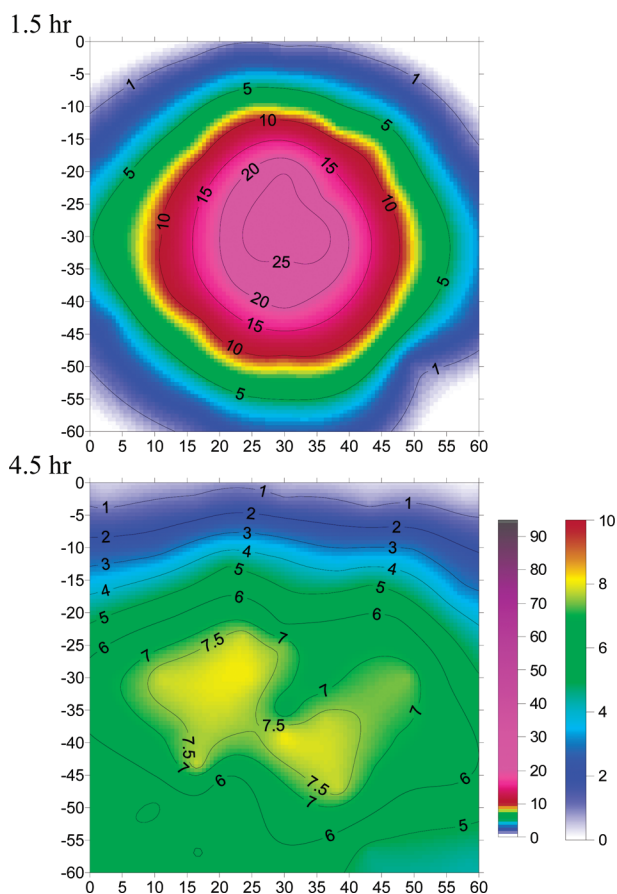
According to the MeI degradation experiment, the first-order degradation rate constant was  $0.0779 \text{ h}^{-1}$ , giving a half-life of 8.9 h. The half-life was shorter than those measured by Gan et al. (11–43 d for the unamended soils with 0.92–2.99% organic matter (20)), Zheng et al. (9.1 d for the unamended soil with 0.92% organic matter (22)), and Guo and Gao (7.4–67.9 d for the unamended soils with 0.74–1.10% organic matter (23)). Methyl iodide degradation rate increases with soil organic matter content (20, 23). Chemical reactions, likely nucleophilic substitutions on the soil organic matter, are considered to be predominant pathways of MeI degradation (20). The high organic matter content of the soil (2.5%) together with the added citrus roots (6.0% of the soil by weight) may have promoted the soil degradation rate in this study.

**Spatiotemporal Distribution of MeI in the Soil.** Figure 3 (also see Figure 1 in the Supporting Information) shows that MeI had moved radially from the injection point after injection. At 0.5 h, the soil gas concentration decreased rapidly in response to the increasing distance from the injection point, specifically, from about  $90 \mu\text{g mL}^{-1}$  at the center to about  $1 \mu\text{g mL}^{-1}$  at 20-cm distance (Figure 1 in the Supporting Information). Little MeI reached the soil surface and became available for volatilization at this time. This was also confirmed by the volatilization flux curve (Figure 2). Once the MeI reached the soil surface, it readily entered the air. The gradient of soil gas concentration at the soil surface increased until around 2.5–3.5 h and decreased thereafter (Figure 3; also see Figure 1 in the Supporting Information), again, consistent with the observed volatilization flux (Figure 2). Due to the volatilization, soil gas concentration near the soil surface was comparably lower than the other three edges. As expected, the soil gas concentration in the center of the





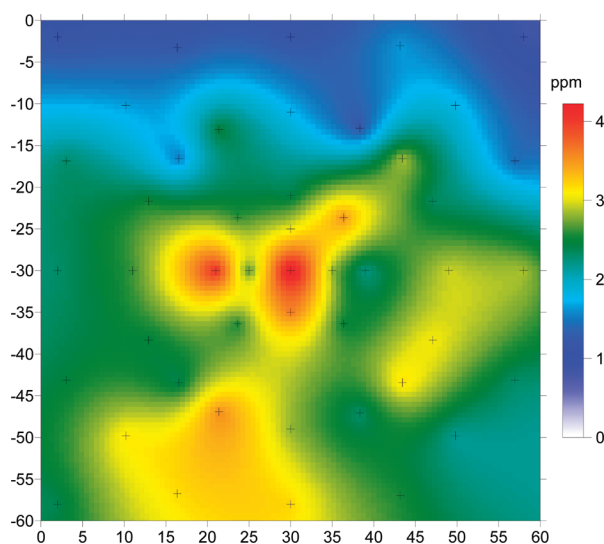
**FIGURE 2.** Mel emission rate and cumulative emission from the soil surface (with a surface area of 60 cm<sup>2</sup>).



**FIGURE 3.** Spatial distribution of Mel gas-phase concentration ( $\mu\text{g mL}^{-1}$ ) at 1.5 and 4.5 h in the soil chamber (60  $\times$  60 cm).

chamber declined rapidly during the first four hours because of the processes of atmospheric volatilization, degradation, and diffusion of MeI into the soil chamber (Figure 3; also see Figures 1 and 2 in the Supporting Information). At a radius of 19 cm from the center, the breakthrough curves of the ports 37–52 showed that soil gas concentration reached a maximum of about  $9 \mu\text{g mL}^{-1}$  at 1.5 h. Due to the surface volatilization, the MeI dissipation within the top half of the chamber (e.g., ports 37–39 and 51–52) was more rapid than that within the bottom half (ports 42–48). At 24 h, according to gas-phase concentration and a gas-phase retardation coefficient of 1.47 for this experiment (24), about 6.8% of the added MeI remained in the soil.

**Mel Degradation and Iodide Concentration.** The degradation rate of a fumigant mainly controls the availability

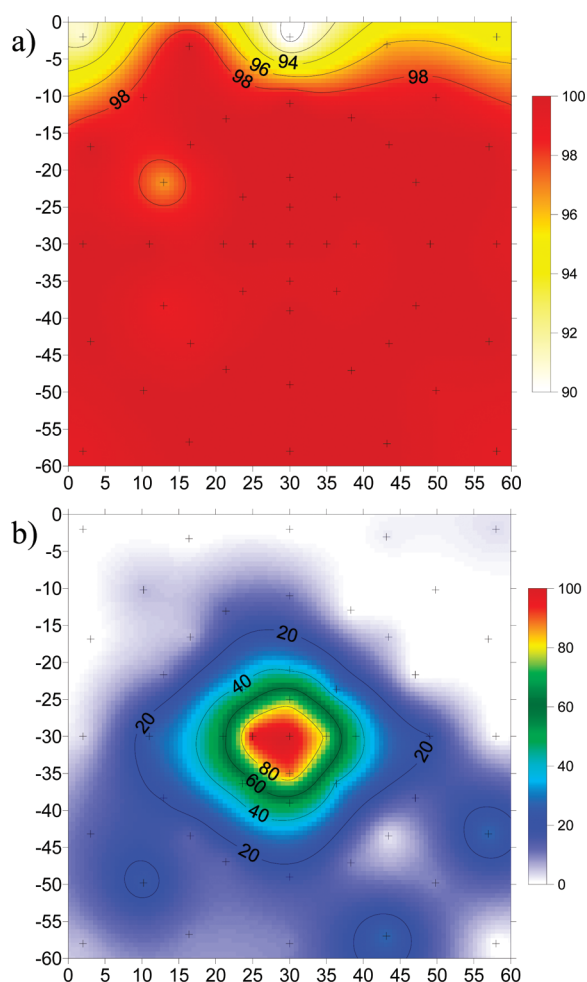


**FIGURE 4.** The spatial distribution of iodide concentration in the soil chamber (60  $\times$  60 cm) after 24-h fumigation. The cross symbols represent the locations of sampling.

of the applied chemical to atmospheric volatilization and the resident soil concentration for pest control. Consistent with gas-phase concentration, the iodide concentration was the highest around the application point and lowest near the soil surface (Figure 4). However, the iodide ion concentration in the soil presented a more irregular pattern than soil gas concentration, indicating a higher degree of variation and experimental uncertainty. For example, the iodide concentration was comparatively high at ports 46, 65, and 66. Based on the iodide concentration, about 43.6% of applied MeI was transformed. Bromide concentration produced after transformation has been used to quantify MeBr degradation in soils and thus to calculate a mass balance (7, 25). Yates et al. (25) found a large number of samples were required to estimate MeBr degradation due to the high variation in bromide concentration. But relatively few studies have measured iodide ion concentration to examine the degradation of MeI in soil and to provide a mass balance estimate. Compared to bromide, the iodide ion is less stable. The generation of  $\text{I}_2$  (gas) is possible when exposed to the light (20). This may contribute to low measured ion concentrations in soil and the uncertainty of using the iodide ion to determine MeI degradation. The degradation ratio was likely to be underestimated due to the high uncertainty and instability of iodide. Luo et al. (24) supported this assumption by comparing measured and simulated results and found the simulated MeI volatilization and spatial distribution of gas-phase concentration were consistent, but the measured degradation ratio (43.6%) was lower than the simulated value (64.9%).

**Mel Control of Barnyardgrass Seed, Fungi, and Citrus Nematode.** Barnyardgrass seed, citrus nematode, and *F. oxysporum* respond differently to MeI. Citrus nematodes were the most sensitive to MeI. After fumigation, few nematodes were alive in the soil except for the surface soil. Near the soil surface, more than 90% of nematodes were killed (Figure 5a). This confirmed that MeI is an excellent nematicide; as has been observed previous studies. For example, Becker et al. (9) reported MeI had high efficacy to control both citrus nematodes and root-knot nematodes, even better than MeBr.

However, the same exposure to MeI had little effect on *F. oxysporum*. In contrast to citrus nematodes, 100% of *F. oxysporum* survived after fumigation. Previous studies also show that *F. oxysporum* is difficult to control by some fumigants (26). Ma et al. (10) found that about 4 times more propargyl bromide was required to kill *F. oxysporum* than

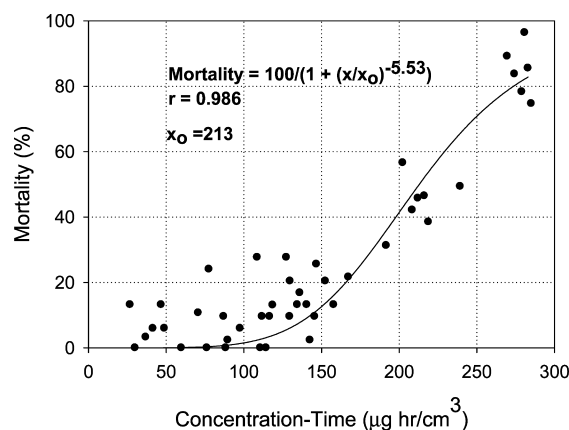


**FIGURE 5.** The mortality (%) of a) citrus nematodes and b) barnyardgrass seeds in the soil chamber (60 × 60 cm) after 24-h fumigation. The cross symbols represent the locations of sampling.

that needed for barnyardgrass seeds. Hutchinson et al. (15) showed that to achieve 50% control of *F. oxysporum*, a CT of 688  $\mu\text{g h mL}^{-1}$  was required for MeI. Another fumigant, chloropicrin, has been found to be effective in controlling fungi. The combination of chloropicrin and MeI is often necessary to improve efficacy toward fungi such as *F. oxysporum* (15). Furthermore, methyl bromide fumigations often included chloropicrin to improve control of fungi.

The efficacy of MeI toward barnyardgrass seeds fell between its efficacy toward citrus nematodes and *F. oxysporum*. Near the injection point, over 80% of the barnyardgrass seeds were controlled by MeI (Figure 5b). The mortality of barnyardgrass seeds decreased rapidly with increasing radial distance from the injection point due to the decrease in the concentration–time index. At a radius of about 10 cm, the mortality was about 40%. At radii greater than 20 cm, few seeds were influenced by the applied MeI, during the 24 h experiment. The CT plotted against the measured seed mortality is shown for 49 ports in Figure 6. A logistic equation was used to fit the curve, resulting in an  $\text{EC}_{50}$  of 213  $\mu\text{g h mL}^{-1}$ . To control barnyardgrass, a CT of greater than 300  $\mu\text{g h mL}^{-1}$  was required. It has been reported that MeI is a more effective fumigant to control weeds than MeBr (14, 27). We believe that at the normal field application rate (about 3 times greater than the MeI rate applied in this study), or with plastic tarps (4), the barnyardgrass seeds should be effectively controlled.

Data and methods to evaluate the environmental effects and pest control efficacy of various pesticide application



**FIGURE 6.** The relationship of concentration–time index (CT) of MeI to the mortality of barnyardgrass seeds in the soil chamber after 24-h fumigation (the curve was fitted based the means of CT and mortality at the intervals of CT < 50, 50–100, 100–130, 130–150, 150–200, 200–250, 250–280, >280).

methods are currently lacking. This study provides a protocol for producing quantitative information on volatile pesticide transport, fate, and efficacy against soil-borne pests. Due to high costs associated with field experiments, investigations of the pesticide and pest behavior by simulating agricultural practices in the laboratory are important to better understand their dynamics processes in the environment. A 2-D soil chamber with a surface-mounted flux chamber was designed to determine volatilization, spatiotemporal distribution of gas-phase concentration in real time, degradation, and pest control of MeI. Using the approach presented in this study, the emission rate, soil gas-phase concentration, and pest control of different volatile pesticides can be compared under various treatments, such as less permeable films, surface irrigation, organic matter, and ammonium thiosulfate addition. Besides fumigants, this approach can also be used to study the emission rates and dynamic processes of other volatile organic compounds or greenhouse gases as well as effects of their management practices in the porous media. A diurnally varied, rather than constant, temperature regime can be used to better represent the field conditions with regard to pesticide transport, fate, and pest survivability in the future study (4). Further research will be necessary to compare pesticide transport and pest responses under laboratory and field conditions.

## Acknowledgments

The authors thank Q. Zhang, F. Ernst, and Y. Wang for their technical assistance in conducting these experiments. The use of trade, firm, or corporation names in this paper is for the information and convenience of the reader. Such use does not constitute an official endorsement or approval by the United States Department of Agriculture or the Agricultural Research Service of any product or service to the exclusion of others that may be suitable.

## Supporting Information Available

Figures show the spatial and temporal distribution of MeI gas-phase concentration ( $\mu\text{g mL}^{-1}$ ) in the soil. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## Literature Cited

- Shorter, J. H.; Kolb, C. E.; Crill, P. M.; Kerwin, R. A.; Talbot, R. W.; Hines, M. E.; Harriss, R. C. Rapid degradation of atmospheric methyl bromide in soils. *Nature (London)* **1995**, *377*, 717–719.

- (2) Yates, S. R.; Ernst, F. F.; Gan, J. Y.; Gao, F.; Yates, M. V. Methyl bromide emissions from a covered field II: Volatilization. *J. Environ. Qual.* **1996**, 25, 192–202.
- (3) Yates, S. R.; Knuteson, J.; Ernst, F.; Zheng, W.; Wang, Q. The effect of sequential surface irrigations on field-scale emissions of 1,3-dichloropropene. *Environ. Sci. Technol.* **2008**, 42, 8753–8758.
- (4) Ashworth, D. J.; Ernst, F. F.; Xuan, X.; Yates, S. R. Laboratory assessment of emission reduction strategies for the agricultural fumigants 1,3-Dichloropropene and chloropicrin. *Environ. Sci. Technol.* **2009**, 43 (13), 5073–5078.
- (5) Gold, L. S.; Slone, T. H.; Ames, B. N.; Manley, N. B. Pesticide residues in food and cancer risk: A critical analysis. In *Pesticide Residues in Food and Cancer Risk*; Krieger, R., Ed.; Academic Press: San Diego, CA, 2001; pp 799–843.
- (6) Gan, J. Y.; Yates, S. R.; Papiernik, S. K.; Crowley, D. Application of organic amendments to reduce volatile pesticide emissions from soil. *Environ. Sci. Technol.* **1998**, 32, 3094–3098.
- (7) Yates, S. R.; Gan, J.; Papiernik, S. K. Environmental fate of methyl bromide as a soil fumigant. *Rev. Environ. Contam. Toxicol.* **2003**, 177, 45–122.
- (8) Gao, S.; Qin, R.; McDonald, J. A.; Hanson, B. D.; Trout, T. J. Field tests of surface seals and soil treatments to reduce fumigant emissions from shank injection of Telone C35. *Sci. Total Environ.* **2008**, 405, 206–214.
- (9) Becker, J. O.; Ohr, H. D.; Grech, N. M.; McGiffen, M. E.; Sims, J. J. Evaluation of methyl iodide as a soil fumigant in container and small field plot studies. *Pestic. Sci.* **1998**, 52, 58–62.
- (10) Ma, Q. L.; Gan, J. Y.; Becker, J. O.; Papiernik, S. K.; Yates, S. R. Evaluation of propargyl bromide for control of barnyardgrass and *Fusarium oxysporum* in three soils. *Pest Manage. Sci.* **2001**, 57, 781–786.
- (11) Wang, D.; Yates, S. R. Spatial and temporal distributions of 1,3-dichloropropene in soil under drip and shank application and implications for pest control efficacy using concentration-time index. *Pestic. Sci.* **1999**, 55, 154–160.
- (12) Yates, S. R.; Knuteson, J.; Zheng, W.; Wang, Q.; Ernst, F.; Ashworth, D. Reducing atmospheric emissions of 1,3-D From large fields using organic amendments. *ASA-CSSA-SSSA Annual Meeting*, Nov 1–5, 2009, Pittsburgh, PA.
- (13) Allaire, S. E.; Yates, S. R.; Ernst, F. F.; Gan, J. A dynamic two-dimensional system for measuring volatile organic compound volatilization and movement in soils. *J. Environ. Qual.* **2002**, 31, 1079–1087.
- (14) Zhang, W. M.; McGriffen, M. E.; Becker, J. O.; Ohr, H. D.; Sims, J. J.; Kallenbach, R. L. Dose response of weeds to methyl iodide and methyl bromide. *Weed Res.* **1997**, 37, 181–189.
- (15) Hutchinson, C. M.; McGiffen, M. E.; Ohr, H. D.; Sims, J. J.; Becker, J. O. Efficacy of methyl iodide and synergy with chloropicrin for control of fungi. *Pest Manage. Sci.* **2000**, 56, 413–418.
- (16) Solomon, S.; Garcia, R. R.; Ravishankara, A. R. On the role of iodine in ozone depletion. *J. Geophys. Res.* **1994**, 99 (D10), 20491–20499.
- (17) Viglierchio, D. R.; Schmitt, R. V. On the methodology of nematode extraction from field samples: Baermann funnel modifications. *J. Nematology* **1993**, 15, 438–444.
- (18) Ashworth, D. J.; Ernst, F. F.; Yates, S. R. Soil chamber method for determination of drip-applied fumigant behavior in bed-furrow agriculture: application to chloropicrin. *Environ. Sci. Technol.* **2008**, 42, 4434–4439.
- (19) Gao, F.; Yates, S. R.; Jin, Y. Laboratory study of closed and dynamic flux chambers: experimental results and implications for field application. *J. Geophys. Res.* **1998**, 103 D20, 26115–26125.
- (20) Gan, J.; Yates, S. R. Degradation and phase partition of methyl iodide in soil. *J. Agric. Food Chem.* **1996**, 44, 4001–4008.
- (21) Gan, J.; Yates, S. R.; Ohr, H. D.; Sims, J. J. Volatilization and distribution of methyl iodide and methyl bromide after subsoil application. *J. Environ. Qual.* **1997**, 26, 1107–1115.
- (22) Zheng, W.; Papiernik, S. K.; Guo, M.; Yates, S. R. Accelerated degradation of methyl iodide by agrochemicals. *J. Agric. Food. Chem.* **2003**, 51, 673–679.
- (23) Guo, M.; Gao, S. Degradation of Methyl Iodide in Soil: Effects of Environmental Factors. *J. Environ. Qual.* **2009**, 38 (2), 513–519.
- (24) Luo, L. F.; Yates, S. R.; Ashworth, D. J. Predicting fumigant transport and pathogen control in soils. *Environ. Sci. Technol.* 2010 (To be submitted soon).
- (25) Yates, S. R.; Gan, J. Y.; Ernst, F. F.; Mutziger, A.; Yates, M. V. Methyl bromide emissions from a covered field I: Experimental conditions and degradation in soil. *J. Environ. Qual.* **1996**, 25, 184–192.
- (26) Minuto, A.; Gilardi, G.; Gullino, M. L.; Garibaldi, A. Reduced dosages of methyl bromide applied under gas-impermeable plastic films for controlling soilborne pathogens of vegetable crops. *Crop Prot.* **1999**, 18, 365–371.
- (27) Hutchinson, C. M.; McGiffen, M. E.; Sims, M. E.; Sims, J. J.; Becker, J. O. Fumigant combinations for *Cyperus esculentum* L. control. *Pest Manage. Sci.* **2004**, 60, 369–374.

ES1002814